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Microbial fuel cells: An overview of current technology

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ABSTRACT

Research into alternative renewable energy generation is a priority, due to the ever-increasing concern of climate change. Microbial fuel cells (MFCs) are one potential avenue to be explored, as a partial solution towards combating the over-reliance on fossil fuel based electricity. Limitations have slowed the advancement of MFC development, including low power generation, expensive electrode materials and the inability to scale up MFCs to industrially relevant capacities. However, utilisation of new advanced electrode-materials (*i.e.* 2D nanomaterials), has promise to advance the field of electromicrobiology. New electrode materials coupled with a more thorough understanding of the mechanisms in which electrogenic bacteria partake in electron transfer could dramatically increase power outputs, potentially reaching the upper extremities of theoretical limits. Continued research into both the electrochemistry and microbiology is of paramount importance in order to achieve industrial-scale development of MFCs. This review gives an overview of the current field and knowledge in regards to MFCs and discusses the known mechanisms underpinning MFC technology, which allows bacteria to facilitate in electron transfer processes. This review focusses specifically on enhancing the performance of MFCs, with the key intrinsic factor currently limiting power output from MFCs being the rate of electron transfer to/from the anode; the use of advanced carbon-based materials as electrode surfaces is discussed.

1. Introduction

Energy generation, storage and consumption are topics that are increasingly prevalent within modern research fields and are of global interest and importance [1,2]. Research into alternative renewable energy generation sources are increasing exponentially, with vast research showing promising results, in an abundance of areas including: solar [3], wind [4], tidal [5], geothermal [6] and biomass energy generation (Fig. 1) [7,8]. Currently no individual renewable energy source has the ability to compete with and replace the conventional fossil-fuel based energy generation approach, however, combining renewable energy sources such as, solar-wind hybrids and/or solar-hydrogen fuel cells may be alternative routes to be explored [9,10].

One potential alternative energy source is the use of microbial fuel cells (MFCs). MFCs follow a similar concept to traditional fuel cells (Fig. 2). However, MFCs utilise the bio-catalytic capabilities of viable microorganisms and are capable of using a range of organic fuel sources, by converting the energy stored in the chemical bonds, to generate an electrical current instead of relying for example, on the use of metal catalysts [1]. Microorganisms, such as bacteria, can generate electricity by utilising organic matter and biodegradable substrates such as wastewater, whilst also accomplishing biodegradation/treatment of biodegradable products, such as municipal wastewater [1,11]. Table 1 provides an overview of the current literature of MFCs. Clearly, significant attention has been given to MFCs cells due to their ambient operating conditions (*e.g.* utilisation at low temperatures) and a variety of biodegradable substrates as fuel. This review aims to highlight the current understanding of MFCs, whilst giving a thorough overview of the field. Particular emphasis is placed upon the fundamentals of MFC technologies, electrode materials, mechanism of electron transport and field standardisation. Further, this review focusses specifically on enhancing the performance of MFCs *via* the optimisation of specific

List of abbreviations: ATP, Adenosine Tri-Phosphate; CNTs, Carbon Nanotubes; COD, Chemical Oxygen Demand; GCE, Glassy Carbon Electrode; HER, Hydrogen Evolution Reaction; MFCs, Microbial Fuel Cells; MWCNTs, Multiwall Carbon Nanotubes; NADH, Nicotinamide Adenine Dinucleotide; NADPH, Nicotinamide Adenine Dinucleotide Phosphate; NER, Normalised Energy Recovery; ORR, Oxygen Reduction Reaction; PBS, Phosphate Buffer Solution; PEM, Proton Exchange Membrane; SEM, Scanning Electron Microscopy; SMFC, Sediment Microbial Fuel Cell; SWCNTs, Single-Wall Carbon Nanotubes; 3D, Three-Dimensional; TEM, Transmission Electron Microscopy; TCA, Tricarboxylic Acid Cycle; 2D, Two-Dimensional

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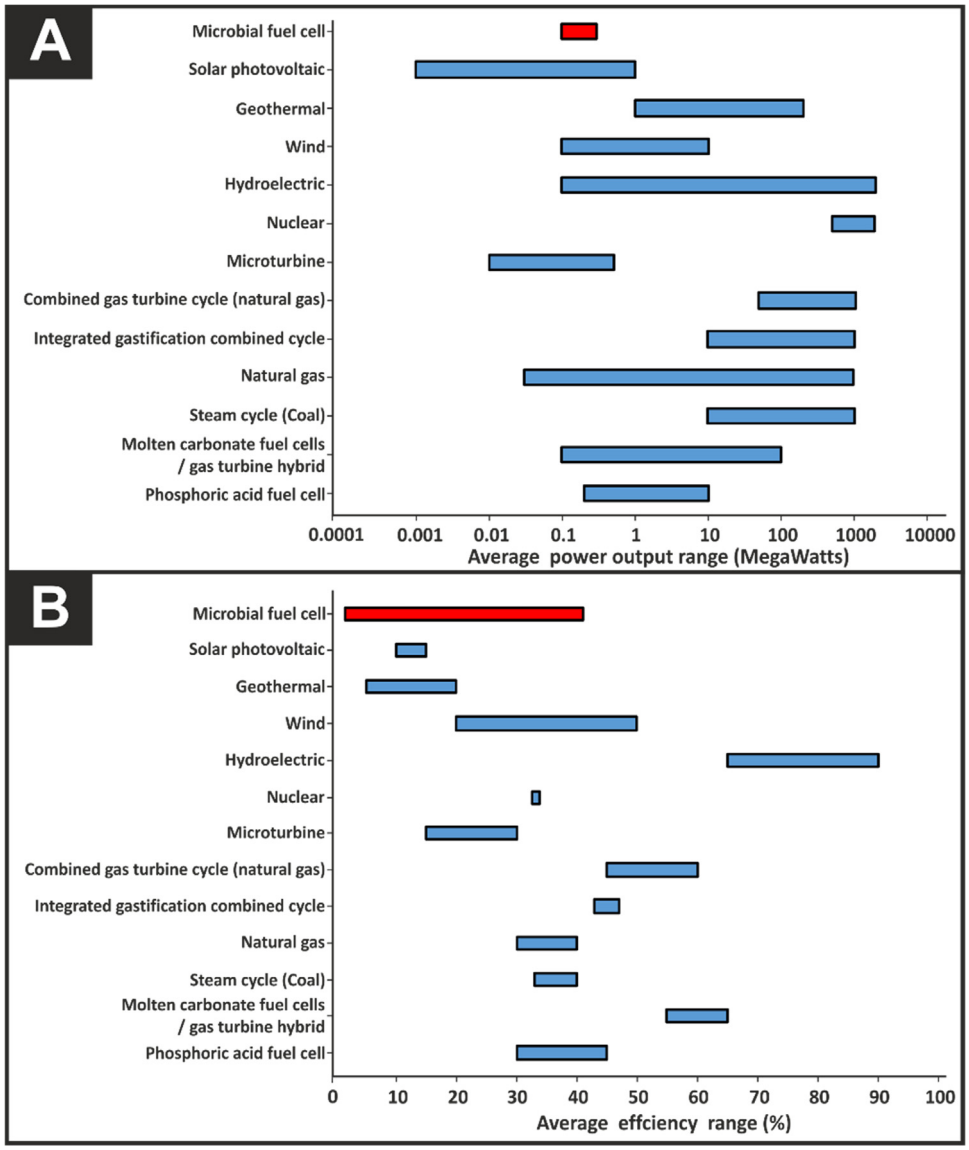

Fig. 1. A) Average power outputs of a range of fuel technologies, including both traditional energy sources (*i.e.* coal and natural gas) and alternative/renewable energy sources. B) Shows the average efficiency range of these fuel sources. Note that MFCs require further and sustained research to compare with other energy sources. Data obtained from [106,112,294–296].

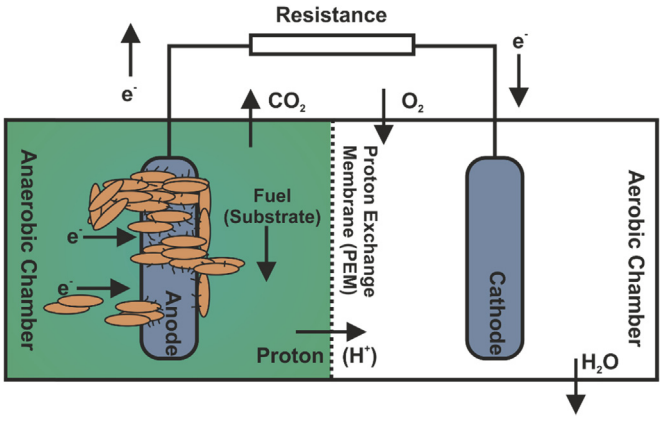

Fig. 2. Schematic of a typically employed two-chamber microbial fuel cell highlighting the various electrochemical and electro-microbiological processes. Figure adapted from reference [1].

parameters, with the hope of highlighting the main limiting factors and bringing them to the forefront of future investigations.

1.1. History of MFCs

The first recorded occurrence of electrochemical activity between bacterial/fungal (yeast) species and electrodes can be traced back to the early 20th century, reported by Potter, where live cultures of *Escherichia coli* and *Saccharomyces* spp., produced electricity using platinum macro-electrodes in a battery type setup with sterile media [12]. This was later confirmed by Cohen in 1931, who reported a voltage of 35 V at a current of 0.2 mA from a stacked bacterial fuel cell system [13]. Although these publications are often referred to as the origin of electromicrobiology, it was not until 1963 when a National Aeronautics and Space Administration (NASA) space program demonstrated the opportunity to recycle and convert human waste to electricity during space flights [14–16]. In 1990, pioneering work from Habberman and Pommer first reported a long-term MFC. In this study, the MFC in question was employed in continuous service, for 5 years (*i.e.* from 1986), utilising municipal wastewater, without malfunction or

Table 1
Overview of the state of the current literature of MFC performance with respect to the variable electrochemical-biology mechanisms and carbon-based electrodes. The best output by an MFC known to date is, 5.61 w m^{-2} (11,200 W m^3) this can be compared to the US national average of solar power which is estimated to be between 100 W m^{-2} and 150 W m^{-2} [174,261]. Note, that in regards to the energy output, the units/benchmarking are not consistent therefore comparison between MFCs is difficult.

Anode material	Cathode material	Microbial composition	Fuel/substrate	Suggested mechanism	Energy output	References
3D few-layer graphene macroporous scaffolds	Glass slide coated with a layer of Cr/Au or Ti/Pt	Mixed community – *Geobacter* spp., enriched	–	Cytochrome c activity	11, 2000 W m^{-3}	[174]
2D monolayer graphene sheet	Glass slide coated with a layer of Cr/Au or Ti/Pt	Mixed community – *Geobacter* spp., enriched	–	Cytochrome c activity	8, 840 W m^{-3}	[174]
Carbon felt	Activated carbon, carbon black and poly (vinylideneflouride) binder	Aerobic mixed community	'High strength' swine wastewater	–	750 ± 70 mW m^{-2}	[262]
Carbon felt	Graphite felt	Anaerobic mixed community	Sludge from domestic wastewater	–	7.07 mW m^{-2}	[161]
Carbon felt	Graphite felt	Anaerobic mixed community	Sludge from domestic wastewater	–	2.34 mW m^{-2}	[161]
Carbon cloth	Carbon cloth/carbon felt	Mixed community	–	Direct – nanowires and c cytochrome	3.5 A m^2	[107]
Graphite felt	Graphite felt	*R. ferrireducens*	–	Direct contact mediated - nanowires	0.57 mA m^2 / 620 mV	[165]
Graphite foam	Graphite foam	*R. ferrireducens*	–	Direct contact mediated - nanowires	74 mA m^2 / 445 mV	[165]
Multilayer graphene coating on stainless steel electrode	Carbon paper	*E. coli*	Glucose	–	2668 mW m^{-2}	[171]
Reduced graphene oxide (particles)	Carbon cloth	Mixed community	Anaerobic sludge from wastewater	–	3.6 W m^{-3}	[172]
Activated carbon modified electrode	Carbon cloth	Mixed community	Anaerobic sludge from wastewater	–	1.7 W m^{-3}	[172]
Reduced graphene oxide (sheets)	Carbon cloth	Mixed community	Anaerobic sludge from wastewater	–	2.7 W m^{-3}	[172]
Glassy carbon coated with MWCNTs	Glassy carbon	*Shewanella oneidensis*	–	–	9.70 μA cm^2	[182]
MWCNTs with hydroxyl groups	Carbon cloth coated with platinum	Mixed community	–	–	167 mW m^2	[184]
Carbon paper	carbon paper coated with Pt catalyst (0.35 mg cm^{-2}; 10% Pt, E-TEK)	*Geobacter* spp,.	Glucose	–	40.3 ± 3.9 mW m^{-2}	[263]
Graphite plate	Graphite plate	*Saccharomyces cerevisiae*	Glucose	–	16 mW m^{-2}	[264]
Carbon paper	carbon paper coated with Pt catalyst (0.35 mg cm^{-2}; 10% Pt, E-TEK)	*G. sulfurreducens*	Acetate	–	48.4 ± 0.3 mW m^{-2}	[263]
Carbon paper	carbon paper coated with Pt catalyst (0.35 mg cm^{-2}; 10% Pt, E-TEK)	*Geobacter* spp,.	Lactate	–	52 ± 4.75 mW m^{-2}	[263]
Graphite	Graphite	*Deltaproteo bacterium*	Marine sediment in acetate	–	14 mW m^{-2}	[265]
Carbon paper	Carbon paper containing either 0.35 mg cm^{-2} of Pt, or 0.50 mg cm^{-2} Pt/Ru (1:1 molar ratio)	*Gammaproteo* and *Shewanella affinis*	Cyctenin	–	36 mW m^{-2}	[266]
Carbon paper	Carbon paper containing a Pt catalyst (0.35 mg cm^{-2}; 10% Pt; E-Tek, NJ)	*Betaproteobacteria*	Ethanol	–	40 ± 2 mW m^{-2}	[267]
Graphite with neutral red (NR)	Graphite coated with a 1 mm thick porcelain septum made from 100% kaolin	*E. coli*	Sewage sludge	–	152 mW m^{-2}	[89]
Graphite with Mn^{4+}	Graphite coated with a 1 mm thick porcelain septum made from 100% kaolin	*E. coli*	Sewage sludge	–	91 mW m^{-2}	[89]
Graphite plates	Graphite plates	Mixed community	Glucose	–	283 Mw m^{-2}	[268]
Composite electrode (graphite/PTFE)	Graphite air-cathode with a Pt/C catalyst layer (40 wt% of Pt)	*E. coli*	Glucose	–	760 mW m^{-2}	[269]
Non-wet-proof carbon paper	Non-wet-proof carbon paper	Mixed community	Cellulose	–	188 mW m^2	[270]
Carbon paper with polypyrrole coated-CNTs	Non-wet-proof carbon paper	*E. coli*	Glucose	–	228 mW m^{-2}	[271]
Teflon treated carbon fibre paper	Graphite plate	Mixed community	Glucose	–	15.2 mW m^{-2}	[272]
Teflon treated carbon fibre paper	Carbon cloth coated with a Pt catalyst (ETEK, 0.5 mg cm^{-2})	Mixed community	Lactose	–	17.2 mW m^{-2}	[273]
Graphite	Graphite	Mixed community	Glucose	–	3.6 W m^{-2}	[274]

(*continued on next page*)

Table 1 (*continued*)

Anode material	Cathode material	Microbial composition	Fuel/substrate	Suggested mechanism	Energy output	References
Graphite fibre brush anodes	30 wt% wet-proofed carbon cloth (type B − 1B, E-TEK) with platinum (0.5 mg cm^{-2})	Mixed community	1 g L^{-1} acetate in 50 mM phosphate buffer	–	1430 mW m^{-2}	[275]
Reduced graphene oxide and polyaniline nanofibers coated onto carbon cloth	Carbon felt	Mixed community	Anaerobic sludge	–	1390 mW m^{-2}	[276]
Reduced graphene oxide coated onto carbon cloth	Carbon felt	Mixed community	Anaerobic sludge	–	1003 mW m^{-2}	[276]
Carbon cloth	Carbon felt	Mixed community	Anaerobic sludge	–	468 mW m^{-2}	[276]
Three-dimensional (3D) reduced graphene oxide–nickel foam anode	Carbon cloth	*Shewanella oneidensis* MR-1	25 mL solution of 50 mM ferricyanide in 100 mM PBS -pH 7.4	–	661 mW m^{-3}	[277]
Hierarchically porous chitosan/vacuum stripped graphene scaffold	Carbon cloth	*P. aeruginosa*	Glucose	Endogenous phenazine mediator	1530 mW m^{-2}	[278]
Multilayer graphene - sponge composite anode with stainless steel current collectors	carbon cloth electrode coated with platinum catalyst	Mixed community	Waste water with glucose	Nanowires observed by SEM – direct transfer	1.57 W m^{-2}	[279]
Multilayer graphene with iron tetrasulfophthalocyanine (FeTsPc)	FeTsPc-graphene cathode (0.2 mg cm^{-2})	*E. coli*	Culture medium (PBS, 10.0 g of peptone, 5.0 g of NaCl and 3.0 g of beef powder L^{-1})	–	817 mW m^{-2}	[280]
Nitrogen-doped graphene	Carbon paper coated with Pt/C or nitrogen	Mixed community	Activated sludge from a municipal sewage treatment plant	–	776 ± 12 mW m^{-2}	[281]
1-(3-aminopropyl)-3-methylimidazolium bromide functionalized graphene nanosheets	Carbon paper	*Shewanella oneidensis* MR-1	18 mM lactate substrate	Outer membrane cytochrome proteins and excreted redox mediators (riboflavin)	601 mW m^{-2}	[282]
Carbon paper	Carbon paper	*Shewanella oneidensis* MR-1	18 mM lactate substrate	Outer membrane cytochrome proteins and excreted redox mediators (riboflavin)	142 mW m^{-2}	[282]
Graphene nanosheets coated onto carbon paper	Carbon paper	*Shewanella oneidensis* MR-1	18 mM lactate substrate	Outer membrane cytochrome proteins and excreted redox mediators (riboflavin)	203 mW m^{-2}	[282]
Carbon paper	Carbon paper	Mixed community	Anaerobic sludge, with glucose	Direct electron transfer	182 mW m^{-2}	[283]
Layer by layer addition of graphene monolayers onto carbon paper	Carbon paper	Mixed community	Anaerobic sludge, with glucose	Direct electron transfer	368 mW m^{-2}	[283]
MnO_2 treated graphite felt	Carbon felt	Mixed community	Sludge and sediment with sodium acetate substrate	–	83 W m^{-3}	[284]
Platinum loaded carbon cloth	carbon-cloth electrode containing 0.5 mg/cm^2 of Pt catalyst (E-Tek)	Mixed community	Waste water with glucose substrate	–	262 ± 10 mW m^{-2}	[88]
Platinum loaded carbon paper	Carbon paper	*Geobacter metallireducens*	Acetate	–	38 mW m^{-2}	[28]
Crumpled graphene coating on carbon cloth electrodes	Carbon cloth	Anaerobic sludge	Sodium acetate	–	3300 mW m^{-2}	[172]
Carboxyl graphene coated onto stainless steel fibre felt	Carbon felt	Mixed community	Acetate	–	2143 mW m^{-2}	[285]
Carboxyl graphene coated onto carbon cloth	Carbon felt	Mixed community	Acetate	–	1018 mW m^{-2}	[285]
Graphene micro-sheets electrochemically exfoliated onto carbon cloth	Graphite rods	Mixed community	Domestic waste water – Glucose	–	2850 mW m^{-2}	[286]
Graphene oxide coated onto carbon cloth	Carbon cloth coated with Pt catalyst (20% Pt/C, E-Tek) at a loading of 0.5 mg cm^{-2}	*E. coli*	Activated anaerobic sludge – sodium acetate	–	1905 mW m^{-2}	[287]
Graphene oxide coated onto carbon cloth	Carbon cloth	*P. aeruginosa*	Glucose	Electron shuttle – pyocyanin	52.5 mW m^{-2}	[159]
Polyaniline/graphene foam coated onto carbon cloth	Carbon cloth	*S. oneidensis*	Lactate	–	768 mW m^{-2}	[270]
Polypyrrole/oxidised graphene coated onto graphite felt	Carbon felt	*S. oneidensis*	Lactate	–	1326 mW m^{-2}	[288]

(*continued on next page*)

Table 1 (*continued*)

Anode material	Cathode material	Microbial composition	Fuel/substrate	Suggested mechanism	Energy output	References
MnO_2/functionalised graphene nanosheets	Stainless steel net with wet-proof gas diffusion layers, and a catalyst layer (86 wt% activated carbon powder, 12 wt% PTFE, and 2 wt% acetylene black powder, containing 5 mg cm^{-2} MnO2/GNS catalyst)	Mixed community	Anaerobic sludge – Acetate	–	2083 mW m^{-2}	[289]
Graphene oxide/SnO_2 composites coated onto graphite	Platinum rod	*E. coli*	Glucose	–	1624 mW m^{-2}	[290]
MWCNTs coated onto carbon cloth	Carbon cloth coated with CNTs or Carbon cloth coated with CNTs and 0.5 mg cm^{-2} of Pt catalyst or Carbon cloth coated with CNTs and 0.5 mg cm^{-2} of Pt catalyst and PEM fused directly	Mixed community	Domestic wastewater – Acetate	–	65 mW m^{-2}	[291]
Graphene/TiO_2 composites coated onto carbon paper	Carbon paper	*S. oneidensis*	Lactate	–	1060 mW m^{-2}	[292]
Graphene oxide/CNTs coated onto hydrogel	Carbon cloth	*E. coli*	Glucose	–	434 mW m^{-2}	[293]

Key: CNTs – carbon nanotubes; MWCNT – multi-walled carbon nanotube; N/A – not available; PBS – phosphate buffer solution.

maintenance [11]. Further, this study for the first time reported indirect electron transfer (a mechanism of electron transfer, which allows specific bacteria to donate electrons) *via* soluble mediators, the example in this study was sulphate/sulphide [11]. To the best of the authors' knowledge, this study was also the first time that the treatment of domestic wastewater was reported [11,17]. In 1999, it was discovered that mediators were not an essential component within MFC configurations, this allowed MFCs to be developed without the need for expensive mediators [18–20]. Following this, an exponential increase in interest occurred within the field of electromicrobiology research, which now boasts over a thousand energy-generation-cells reported in the literature, and the first commercial prototypes are expected soon [21].

1.2. Fundamental bioelectricity generation in MFCs

The development of a bio-potential, due to the bacterial metabolic activity in the anodic compartment (*i.e.* reduction reactions, generating both electrons and protons), and electron acceptor conditions in the cathode (which are separated by a membrane), leads to the generation of bioelectricity in MFCs [22,23]. In the anodic compartment, the electrochemically active microorganisms can donate electrons to an anode, which are liberated by oxidising organic/inorganic waste (*e.g.* the fuel), thus producing a source of energy [1]. An example of an oxidation reaction that takes place by electrochemically active bacteria in the anodic compartment, using acetate as a fuel source can be summarised as [24]:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \quad (1)$$

Electrochemically active microorganisms capable of donating electrons have been previously defined by Logan as exoelectrogens [25]. Other synonyms used throughout the literature include, anode respiring bacteria, [26] electrochemically active bacteria [27,28] and electricigens [29,30]. Microorganisms capable of accepting electrons have been termed, exoelectrotrophs [31,32]. Protons produced *via* the electrochemically active bacteria in the anode diffuse through a half-cell separator (*e.g.* proton exchange membrane (PEM)) into the cathodic compartment. In the cathodic compartment, oxygen is primarily used as the oxidant, due to its abundance and high reduction potential [33,34]. However, the oxygen reduction reaction (ORR), remains one of the contributing bottleneck factors which is inhibiting further optimisation and therefore improvement of MFC configurations, due to both high over-potentials and low kinetics observed [33,35]. Other studies have shown the application of metal oxidants in the cathodic compartment, examples include, copper, cadmium and chromium [35–40]. Once the protons have diffused through the PEM into the cathode they can combine with oxygen that is present, leading to the generation of water *via* the following oxygen reduction reaction (ORR), which can be summarised as [41,42]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

In order to be classified as an MFC, a device must be capable of having its fuel source, which is oxidised at the substrate-anode interface (*e.g.* wastewater), replenished either intermittently or continuously, otherwise the system is not referred to as a MFC, but rather, it is biobattery [24]. The majority of MFC configurations are often utilised as anaerobic devices. This is due to the anaerobic conditions required by bacterial species' currently seen as the "gold standard" in regards to electron transfer properties *e.g. Geobacter sulfurreducens* [21].

MFCs are routinely operated as closed-system devices, where the anodic compartment is kept under anaerobic conditions. This is required in order to facilitate the growth of obligatory anaerobic bacteria capable of electron transfer, such as *G. sulfurreducens* [21]. To date, fuel sources with bacteria that have been identified as being capable of partaking in electron transfer include wastewater, marine sediment soil, freshwater sediment, soil and activated sludge (Table 1) [43,44].

Bacteria in such systems are able to produce electrons by oxidising substrates that are isolated in the anodic compartment. These electrons flow from the anode to the cathode (positive terminal) *via* an external circuit, this leads to the production of electricity due to the difference in potential coupled to the electron flow [24,45]. Protons that are produced at the anode are able to migrate through the solution and across the PEM [46]. PEMs are the most frequently used separators in MFCs due to their desirable properties such as, high conductivity to cations, selective permeability to protons, low internal resistance and the ability to undergo long periods of inactivity without having a detrimental effect on the MFC [47–49]. Once at the cathode, the electrons are able to combine with both protons and water to form oxygen. Currently, the maximum power densities that microorganisms are theorised to be capable of producing have not yet been reached. Theoretically, a single *Escherichia coli* cell that replicates twice every hour with a volume of 0.491 μm^3 has the potential to produce *ca.* 16,000 kW m^{-3} [50]. Depending on the energy gain by the bacteria and the loss of energy at the cathode, a voltage of between 0.3 V and 0.5 V is usually obtained when using energy sources (fuels) such as glucose and acetic acid [50]. The current produced from a MFC is dependent on the rate of substrate biodegradation, whilst the maximum theoretical cell voltage also known as the electromotive force, is dependent on the Gibbs free energy (a thermodynamic quantity equal to the enthalpy of a system, plus the temperature and entropy) of the overall reaction [51]. This can be calculated as the difference between the standard reduction potentials of the specific anodic substrate and the cathodic oxidant [17,24,52]. However, a MFCs electromotive force does not factor in internal losses (*i.e.* resistance) and therefore experimental values are subsequently always significantly lower than theoretically obtained values [24,51].

Most modern MFC technologies developed thus far utilise wastewater as a fuel source, working on the basis of recovering energy *via* the biodegradation of organic-rich waste [1]. The ability to generate electricity from wastewater could play a pivotal role in the production of renewable energy. In 2012, it was reported that 5% of the USA's total energy consumption was used to facilitate water and wastewater treatment facilities [53]. However, for the adequate treatment of wastewater (to relevant regulations and standards), issues surrounding the effluent quality of MFC treated wastewater are yet to be addressed sufficiently [54]. The treatment of wastewater by MFCs alone, may not be a viable option due to stringent effluent quality requirements [54]. Therefore, the addition of other steps such as MFCs integrated with membrane technology and conventional treatment technology (post MFC stage) may also be required [54–56]. MFCs offer a significant advantage over other renewable energy sources, as they can be applied towards wastewater treatment. Another advantage of MFC technologies is it is less dependent in comparison to other renewable energy technologies (*i.e.* solar and wind) upon geographical location and seasonal change [17]. Ye et al. [57] have previously demonstrated a sediment MFC which was capable of power output in temperatures ranging from 4 °C to 35 °C. Further, MFCs can generate hydrogen from the fermentation of sugars in wastewaters, which can then in turn be utilised as a fuel source in other renewable energy technologies [29]. Oh et al. [58], investigated hydrogen production from food processing wastewaters in conjunction with electricity production.

The model bacterial species currently used in MFCs are iron-reducing species such as *Shewanella* spp., and *Geobacter* spp [25]. These bacteria have the ability to degrade organic matter for nutrient cycling, for example iron oxides found in both soil and sediments [59]. Graphite macro-electrodes (unpolished; grade G10, geometry: sticks) have been used to grow such bacterial species as *G. sulfurreducens*, where acetate was used as an electron donor (2 mM) [60].

1.3. Structural configurations

The structural configuration of MFCs varies considerably, ranging from single and two-chamber configurations and with or without the utilisation of a PEM [46,61,62]. Fig. 2 provides a schematic presentation of a typically utilised MFC configuration which comprises of two-chambers, an anodic chamber and a cathodic chamber which are connected by a half-cell separator, with the most commonly utilised separators being, PEM's, salt bridges and ceramics [41,63,64]. This allows protons to move freely to the cathode due to a potential gradient, whilst inhibiting the diffusion of oxygen (or the electron acceptor utilised in the cathodic compartment) to the anode where it can have a potential detrimental effect on the bacteria present.

The structural design of the compartments can vary dramatically in order to enhance power outputs of MFCs. Two-compartment MFCs are typically utilised with a defined medium (such as glucose or acetate) and ran in batch mode. MFCs can also be operated in a continuous mode) and are currently used in laboratories to optimise MFC power outputs [1]. Examples of two-compartment MFC designs include, conventional rectangular shaped MFCs, [1,65,66] cylindrical shaped MFCs, [67–70] miniature MFCs, [71–73] up-flow mode configurations [74,75] and flat plate MFCs [76,77].

Miniature MFCs are receiving considerable attention in both fundamental and applied studies, due to their intrinsic advantages [71]. Miniature MFCs are capable of generating electricity at the millilitre to microlitre scale [71]. One example of a miniaturised MFC has been demonstrated by Mink et al [78]. In this study, a MFC was fabricated with a graphene anode and an air cathode, with a working volume of 25 μL, whilst utilising human saliva as a fuel source [78]. This configuration produced a maximum current density of 1190 A m^{-3}, this was higher than any previous air-cathode micro-sized MFC [78]. Interestingly, in this study, the utilisation of graphene resulted in a 40 times increase in power than that of the carbon cloth control [78]. These findings could potentially result in saliva-powered appliances, utilising MFC technology for both Lab-on-a-Chip and point-of-care diagnostic devices [78]. Further, miniature MFC configurations have shown potential promise as power sources for long-term underwater or littoral autonomous sensors, as MFCs can scavenge nutrients from the environment allowing for the electrogenic biofilm to be sustained at the anode [1,79]. Miniature MFC configurations would be particularly beneficial in isolated regions as Ringeisen et al. have shown that the power output of MFCs is more sensitive to diffusion distance through the PEM, rather than electrode size, thus allowing for more effective power outputs in miniaturised configurations [80].

Up-flow mode MFC configurations have received vast attention, due to their increased suitability for application in wastewater treatment, due to their relative ease to scale-up to industrially relevant sizes [1]. Min and Logan developed the flat plate MFC, in order to replicate the parameters utilised in traditional hydrogen fuel cells, where the electrodes are usually combined into a single strip separated by a PEM; thus allowing the electrodes to be kept in close proximity to enhance proton conduction between the two electrodes [76]. However, in the case of MFCs, PEMs such as Nafion are often utilised which are permeable to oxygen, this could have a detrimental effect on obligate anaerobes if used as the bacteria of choice in the anodic compartment [76]. Therefore this prototype was tested to evaluate if the design was more beneficial than the risk of oxygen permeation to the anode [76]. The results from this flat plate MFC configuration showed a maximum power density of 72 mW m^{-2} when domestic waste water was utilised as the fuel source, this represents a 2.8 times increase in power output when compared to that of a single chambered MFC design, tested by the same research group [76]. Other structural configurations have been utilised throughout MFC technologies, and designs such as tubular configurations have been developed and shown to be advantageous towards increasing power outputs [81,82].

Sediment microbial fuel cells (SMFCs) have been intensively explored for energy generation from natural sediment, with recent focus in particular on their application for wastewater treatment [83]. SMFCs produce electrical current from the organic matter content of sediments using bacterial metabolism. SMFCs differ from other MFCs due to their

essentially complete anoxic conditions at the anode and their membrane-less structure, where the sediment/water interface acts as the membrane [84,85]. However, SMFCs have been criticised, as such set ups are unlikely to generate considerable amounts of electrical energy in order to compete with other energy sources. This is due to their reported limitations, such as large internal resistance and issues arising from scaling up, as increasing electrode size can result in a decrease in power density [83,86]. Despite this, research into SMFCs has intensified recently due to their realised dual functionalities allowing for electricity generation and wastewater treatment *via* the removal of specific contaminations [83]. A study in 1989, using a non-corrosive stainless steel mesh that was plated with platinum black and utilised as the anode, produced a current density of (*ca.* 60 μA cm^{-2}) with *Enterobacter aerogenes* [87].

Due to their complex architectural designs, it is difficult to scale up two chambered MFC configurations [1]. Single chamber configurations offer simpler designs and eliminate the need for a cathodic chamber, as the cathode is exposed directly to the air [1]. This allows for greater financial efficiency, due to the lack of requirement for a cathodic compartment and electron acceptors. Note, because passive oxygen transfer to the cathode does not require air sparging of the catholyte, which is an energy intensive process, this further reduces financial expenditure [88]. The protons produced in the anodic compartment are transferred from the anolyte solution to the porous air-cathode [88]. The first reported single chamber MFC was developed in 2003 by Park and Zeikus [89]. This comprised of a rubber bunged bottle with a centrally-inserted anode and a window-mounted cathode which contained an internal proton-permeable porcelain layer, when sewage sludge was used as the biocatalyst, a maximum power density of 788 mW m^{-2} was obtained [89].

In order to attempt to scale up MFC technologies to an industrially-relevant level, it has been previously demonstrated that a miniaturisation and multiplication approach is one viable route to scale up power output, as opposed to merely increasing the reactor size [90–93]. In light of this, stacked MFCs have been developed. Stacked MFCs allow multiple, individual MFCs to be connected in series or parallel allowing power outputs produced to be enhanced [94]. Aelterman et al. connected six individual continuous MFC units and produced a maximum hourly average of 258 W m^{-3}, whilst utilising a hexacyanoferrate cathode and identical graphite granule electrodes (type00514, diameter between 1.5 and 5 mm, Le Carbone, Belgium) [94]. However, Oh and Logan revealed that when multiple MFCs are stacked together a charge reversal can occur and this can result in a reverse in polarity for one or more of the cells and a reduction in power outputs [95]. Voltage reversal generally occurs when one or more cells in a stacked MFC configuration experiences a more extreme condition (with one example being fuel starvation) compared to the other cells [95]. More specifically, this phenomenon occurs when excessive current is drawn from the fuel cell, at a higher rate than its fuel delivery can support, subsequently this leads to an increase in the anode potential and thus voltage reversal occurs [94].

Other conditions that can result in voltage reversal and therefore impair power outputs include, lack of oxygen at the cathode, impedance differences, lack of a catalyst and insufficient fuel [95]. However, a number of studies have demonstrated MFC stacks that have overcome this issue [95–97]. One example of this is by short-circuiting a cell demonstrating voltage reversal, researchers have used diodes connected in parallel in a hydrogen fuel cell due to their low ohmic resistance, therefore when one or more of the cells are defective, the MFC can automatically short-circuit [95]. Avoiding fuel starvation *i.e.* ensuring there is sufficient substrate at the anode and oxygen at the cathode (for air-cathodes) has also been shown to reduce the possibility of voltage reversal [95]. Further, operating the MFC configuration at lower current densities has also shown to inhibit voltage reversal [95].

One material with the potential of advancing the field of MFCs are ceramics [98,99]. Research thus far demonstrates that when this material is used as a half cell separator, results obtained are comparable to more conventional ion exchange membranes, with the added benefit of being considerably less expensive [98]. The first demonstration of ceramic materials utilised in a MFC configuration was reported in 2003 by Park and Zeikus [89]. In this study, a proton permeable porcelain separator was employed and positioned between graphite electrodes [89]. The graphite electrodes contained surface bound mediators, with the anode containing Mn^{4+} and the cathode Fe^{3+} [89]. With *E. coli* as the biocatalyst the maximum current density and power density were, 1750 mA m^{-2} and 788 mW m^{-2}, respectively [89]. The use of ceramic membranes has allowed for MFCs to be used in field trials, with one example being by Ieropoulos et al. [100]. In this study, the application of ceramic membranes allowed the cost of the structural materials to be decreased to as low as 4.14 GBP per m^2 [101]. This is directly comparable with conventional cation exchange membrane, which in 2016 cost 79.17 GBP per m^2 [101].

In order to increase and optimise the efficiency of MFCs utilising ceramic materials, it is stipulated that varying the ceramic type (with one example being earthenware), the porosity of the clay and the thickness of said ceramic could lead to an increase in power output [98]. Ceramic electrodes have also been developed, as well as ceramic chassis/housing units, this is beneficial, as it would allow the manufacturing process to be simplified, as the entire unit could be manufactured and kilned simultaneously [98,102]. Throughout the literature there are many studies, which describe the coating of ceramics with conductive materials [98]. An example of this has been demonstrated by Thorne et al. in this study porous ceramic electrodes were developed by coating macroporous titanium dioxide ceramics with a thin layer of fluorine-doped tin oxide, by chemical vapour deposition [103]. The power density obtained by the modified ceramic electrodes was around 16 times higher than the best performing carbon anode [103].

1.4. Limiting factors

The limiting factors of MFCs are reported to be high-associated costs (most notably due to electrode materials and the use of PEMs), low energy outputs and limited life spans; the key intrinsic factor currently limiting the power output of MFC technologies is the rate of electron transfer to the anode and the electrochemical properties of the material [104]. Further, the PEM has been shown to be the main source of internal resistance (R_{in}) of MFCs [23,28,105]. In light of these limiting factors, MFCs are currently unable to attain their theoretical power outputs and therefore implementation of this technology into industry is not yet feasible.

The overall efficiency and performance of a MFC can be effected by a vast array of factors as depicted in Fig. 3. Other performance-limiting factors have arisen whilst trying to enhance the performance of MFC for industrial and social applications, these include biofouling (leading to electrode surface blockage and ultimately a reduction in surface area), catalyst inactivation (if present) and excessive biofilm growth - possibly leading to the production of non-conductive debris (Fig. 3) [106]. The production of non-conductive debris such as polymeric substances and/or dead cells, can isolate the electrochemically active biofilm from the electrode surface or with more porous electrodes become entrapped in the 3D architecture; leading to a potential reduction in available surface area and ultimately a reduction in current generation [106–108]. A study conducted in 2017, used cell viability counts and field emission scanning electron microscopy analysis to show that an increase in high polarization resistance correlated with the formation of a dead layer of cells [108]. Further, this study also revealed that the use of ultrasonic treatment was a verified method of controlling biofilm thickness and enhanced cell viability, maintaining stable power generation [108].

There have been other biofilm related factors that are thought to contribute to the performance of a MFC. In a study conducted by Sun et al. [109], it was revealed that when the predominant bacteria in an MFC set-up was *Geobacter anodireducens*, a two-layered biofilm

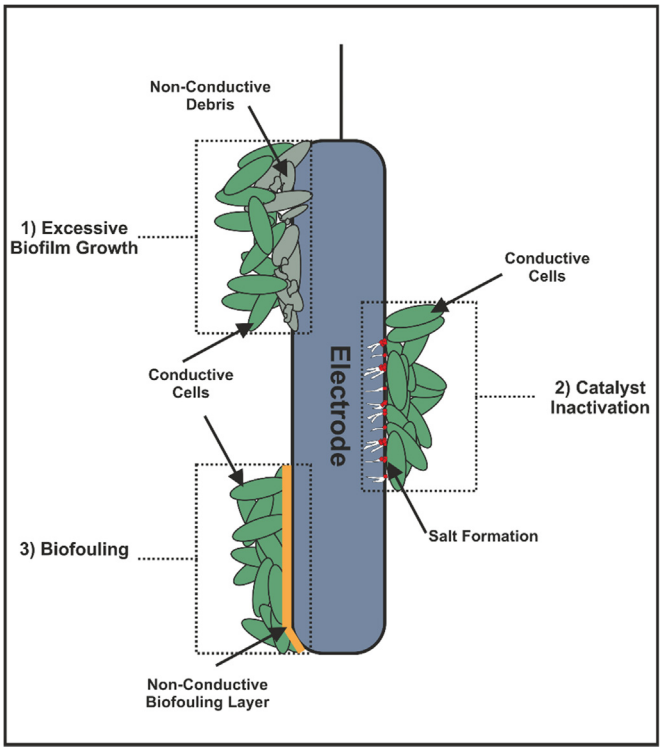

Fig. 3. A schematic depicting a number of ways in which performance of MFC technologies can degrade. Examples here include biofouling (electrode blockage), inactivation of catalysts and excessive growth of bacterial biofilms leading to the production of non-conductive debris.
Figure adapted from [106].

developed over time, with an inner dead core and an outer layer of live cells. Results suggest that the outer layer was responsible for current generation and the dead inner-layer continued as an electrically conductive matrix [109]. It could be speculated that this continued electrochemical activity could be dependent upon the mechanism of electron transfer, for example *Geobacter* spp., are well known for their electrochemical activity due to nanowires - which may still have a viable connection to the electrode surface, even through the non-conductive debris.

Other attributing factors which can have a detrimental effect on both the power outputs and the efficacy of a MFC is the inactivation of electro-catalysts (if present) and the crossover of organic compounds or electron acceptors from the anode to the cathode (and *vice versa*). The crossover of electron acceptors from the cathodic compartment into the anode has been shown in a previous study to disrupt biofilm formation and lead to biofilm inactivation, which can considerably decrease MFC performance, due to the flow of internal currents and the formation of mixed potentials (*i.e.* a system that is short-circuited) [110,111].

1.5. Optimisation of MFC power outputs

The power output obtained *via* MFC technologies can be improved by a number of ways (Table 2):

The introduction of a magnetic field to living microorganisms produces a phenomenon known as the magnetic biological effect [121]. This effect has been shown to induce a series of biological reactions in microorganisms, for example, magnetic fields effect DNA, enzymes and organisational structure of biofilms, which in turn can lead to an alteration in the metabolism of the microorganism [122,123]. The introduction of a high static magnetic field inhibits the physiological processes in microorganisms, whilst the use of lower static magnetic fields promotes microbial activity/growth [124]. In one study, the

Table 2
Possible mechanisms by which to improve the power output.

Mechanism	Refs.
Architectural design of the MFC setup	[112]
Alternative electrode material selection	[113]
Improvement of the cathodes (viable alternatives to platinum)	[114]
Closer-spaced electrodes (leading to a decrease in ohmic resistance)	[115]
Solution selection (allowing for increased conductivity)	[116]
Addition of substrates (more acquiescent to energy production)	[21]
Enhancement of appropriate fuel source	[117,118]
Introduction of a magnetic field to MFC configurations	[119,120]

application of a 100 mT magnetic field increased electricity production of *Shewanella*-inoculated MFCs, leading to an increase in the maximum voltage by 20–27% [125]. This improvement in electricity production has mainly been attributed to enhanced bioelectrochemical activity, possibly due to the induction of oxidative stress mechanisms [124,125].

The introduction of a magnetic field has also been shown to affect the bioelectrocatalytic transformations of several enzymes on the electrode surface, resulting in accelerated electron transfer at the electrode-solution interface [126–128]. Yin et al. reported that the utilisation of magnetic fields (in the range of 0 mT, 100 mT, 200 mT and 300 mT) led to a decrease in start-up periods of the MFCs, with the 100 mT needing the least amount of time (7 days) to obtain a stable voltage output [119]. Further, the maximum power density reported, was produced by the MFC under a 200 mT magnetic field (1.56 $W\,m^{-2}$) compared to the control MFC with no magnetic field (1.19 $mW\,m^{-2}$) [119]. However, the MFC subjected to a 300 mT magnetic field, produced a power density of 0.99 $W\,m^{-2}$. Therefore, it was suggested that there is an optimal intensity magnetic field range, and this could be dependent on the microorganisms utilised in MFC configurations [119]. Thus, it may be noted, that the influence of the magnetic field on the cathode of an MFC setup (due to its effect on the electrical behaviour towards the ORR) needs to be explored comprehensively in order to optimise this method for application within MFCs [119,129,130].

Other studies have reported that the utilisation of low static magnetic fields ($\leq$ 220 mT) improved the cell performance of a MFC demonstrating that the MFC under a 220 mT magnetic field resulted in the best output voltage (756 mV),compared to the control MFC which had no magnetic field (360.1 mV). The use of higher magnetic fields with MFCs, such as 360 mT have been shown to exhibit negative effects upon cell performance. This may lead to a decrease in biomass, lowered maximum voltage (171.8 mV) and lower pollutant removal in the case of residual ammonia nitrogen (84.6 $\pm$ 0.5 $mg\,L^{-1}$) [120]. It is apparent that before magnetic fields can be used to optimise MFCs, comprehensive studies must be undertaken in order to optimise this technique.

The use of catalysts and electron acceptors in MFC configurations is non-essential and their use is often expensive due to the constant need to replenish exhausted materials. In order to avoid expensive costs associated with the use of catalysts/electron acceptors in the cathodic compartment, research interest is currently directed to replacing these materials with microorganisms, known as biocathodes, which can assist and improve cathodic reactions [131]. Both aerobic and anaerobic biocathodes have been explored, this is of paramount importance depending on the terminal electron acceptor adopted in the cathode. One example of an aerobic biocathode is *Thiobacillus ferrooxidans*, and this bacteria has been shown to regenerate ferric ions, which have been utilised as electron mediators in the cathodic compartment [131]. An example of an anaerobic biocathode is *Geobacter metallireducens* which has the ability to oxidise ammonia and reduce nitrate (to nitrogen), leading to denitrification in an MFC configuration [131].

2. Electrode materials

One area which could potentially be explored in order to optimise power output from MFCs, are the electrode materials themselves. In order for a material to be effective as an electrode, it should have a number of properties. It should ideally be economical and exhibit beneficial electrochemical properties (*i.e.* favourable electron transfer) whilst being mechanically stable, in conjunction with a large surface area, giving rise to large current densities.

2.1. Materials

The electrode material is a major constituent of a MFC, determining both the performance and the cost [132]. One of the key areas of current research in electrochemistry is to develop new materials in order to replace platinum [133]. The urgent need to replace platinum is due to the increased global demand as this is a crucial resource within a plethora of industries, with major applications in catalysts, electronics and electrodes [133]. This, combined with an inadequate supply (approximate annual global supply is about 200 Mg (metric ton)), has led to a price surge in platinum making it extremely expensive [133,134]. Platinum may not be suitable as an electrode material for application within MFCs, as this metal has shown antimicrobial properties which lead to the inhibition of *E. coli* division, due to products produced (cisplatin) from a platinum electrode during electrolysis [135]. In light of this, carbon materials and non-corrosive metals are currently the most widely used base electrode materials in MFC configurations, as these materials meet the above requirements (Table 1) [136]. The selection and optimisation of suitable electrode materials is essential in order to increase power outputs from MFCs, as the selected material has been shown to have a significant influence on the release, transfer and acceptance of electrons between the electrodes and the bacteria [132,137,138].

2.2. Electrode topography

Electrodes utilised in MFCs not only function as conductors, as with traditional fuel cells, but the anode material also acts as a support for bacterial biofilms and therefore must be biocompatible with the bacterial cells present. A high surface area is desirable, and a relatively rough surface is thought to be an ideal surface property in a MFC configuration, as it helps with the retention of the bacteria to the surface [136]. Surface roughness/area of the electrode materials has also been shown to play an important role in the generation of electricity [139]. Walter et al. demonstrated that increasing the total anodic surface area, within a fixed volume chamber resulted in an increase in volumetric power density of the MFC [139]. Ye et al. demonstrated that when two glassy carbon plates were polished to uniform roughness in the order of magnitude of 10′s to 100′s of nanometres, after 275 h of experimentation, the (relatively) rougher electrode surface produced higher power densities than its smoother counterpart. Surface roughness is a vital parameter that needs appropriate consideration when selecting electrode materials [140].

2.3. Oxygen reduction reactions

Another potential avenue to explore when trying to enhance power density outputs of the MFCs is improving the oxygen reduction reaction (ORR). This takes place in the cathode (compared to the hydrogen evolution reaction (HER) in microbial electrolysis cells (MECs)) [141]. One way to optimise electricity output is to utilise electro-catalysts or electrode materials that exhibit enhanced electrochemical properties, such as boron nitride and molybdenum disulphide. These materials possess the ability to reduce the over potential of the key electrochemical reaction, leading to a marked improvement in efficiency [49,142–144].

Feng et al. reported that a nitrogen-doped graphene catalyst (of 2–8 layers) gave rise to the oxygen reduction reaction at facile potentials, comparable to that of a platinum catalyst, therefore in a MFC configuration this could give rise to beneficial outputs of the MFC [145]. The advantages of nitrogen-doped graphene include being less expensive than platinum with improved long-term operational stability in comparison to commercial platinum electrodes as measured within alkaline electrolytes [145,146].

Another example of utilising catalysts to improve the ORR in MFCs has been demonstrated by Li et al. [147] using iron and nitrogen functionalised graphene sheets (Fe-N-G, *ca.* > 2 μm), which were more disordered than pristine graphene. The sheets were synthesised and utilised as a non-precious metal catalyst for use within a single-chamber air-cathode MFC. This MFC comprised of a cylindrical anode chamber (5 cm diameter and an effective volume of 40 mL), a cation exchange membrane and carbon felt electrodes [147]. The catalysed cathode was placed at a distance of 1 cm from the anode, with its waterproof layer facing towards air [147]. It was found that when used with MFCs, the Fe-N-G catalyst obtained the highest power density (1149.8 mW m^{-2}) in comparison to a pristine monolayer graphene catalyst control, (561.1 mW m^{-2}) and a commercial Pt/C catalyst (109 mW m^{-2}) [147].

2.4. Capacitive layers

Capacitive bioanodes have been trialled in MFC configurations [148–151]. In one study by Deeke et al. [148], a capacitive layer was coated onto a current collector (plain graphite plate electrode). This consisted of a mixture of activated carbon and a polymer solution, consisting of *N*-methyl-2-pyrrolidone and poly(vinylidene fluoride), this capacitive bioanode was compared against a plain graphite plate electrode. The cathode utilised in both MFCs was a plain graphite electrode plate. During polarization curves, the capacitive bioanode maximum current density was 1.02 ± 0.04 A m^{-2}, whilst the control electrode reached a maximum of 0.79 ± 0.003 A m^{-2} [148]. During charge-discharge experiments (with 5 min charging and 20 min discharging) the capacitive electrode was able to store a total of 22,831C m^{-2} compared to the control (non-capacitive) electrode 12,195 C m^{-2}. Furthermore, the capacitive electrode was capable of recovering 52.9% more charge during each charge-discharge experiment [148]. This indicated that the application of capacitive electrodes in MFCs allowed for simultaneous production and storage of electricity generated [148].

Research from the same group, showed that variation in the thickness of the capacitive layer had an effect on the efficacy of the electrode [152]. Of the electrodes tested with capacitive layers of, 0.2 mm, 0.5 mm and 1.5 mm, the electrode with a capacitive layer of 0.2 mm out-performed the other electrodes in all studies. This electrode produced a maximum current density of 2.53 A m^{-2} during polarization curves, and during charge-discharge experiments stored a cumulative total charge of 96,013 cm^{-2} [152]. This was the first study to identify a parameter that can determine the performance of a MFC with a capacitor [152].

2.5. Carbon based electrodes

The use of carbon-based electrodes has long been established and has led to the production of vast amounts of analytical and industrial applications, due to carbon's high efficacy in heterogeneous electron transfer kinetics. Fig. 4 offers a schematic detailing the structure of five allotropes of carbon [153]. Since the discovery of graphene, there has been a rapid increase in research interest towards utilising this and other novel 2D-nanomaterials, especially in the field of electrochemistry. Nanomaterials, such as carbon nanomaterials, possess many reported beneficial properties, which potentially make them ideal for electrode materials for use within MFCs. Such properties include a large surface area, enhanced electron transfer and promotion of the adsorption of molecules [154]. As microbial growth on the surface of metal

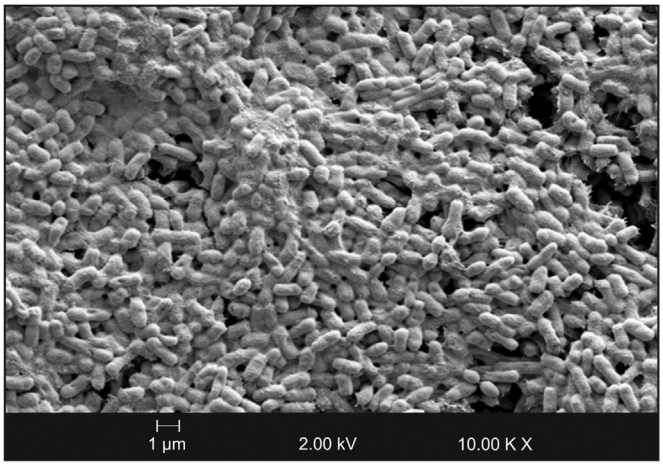

Fig. 4. SEM showing the abundant coverage of an *E.coli* biofilm adhered to the surface of a carbon-paste graphite electrode (courtesy of Whitehead et al. MMU, UK).

anodes can accelerate the corrosion of metals in aqueous solutions, carbon-based electrodes are currently the material of choice for application with MFCs [155,156]. A variety of carbon-based electrode materials have been trialled for use within MFC setups; these include graphite rods [46], carbon felts [157], carbon cloths [136] and carbon meshes [158].

2.5.1. Carbon cloth and felt

Carbon cloth has traditionally been one of the electrode materials of choice for use with MFCs due to its reported useful conductivity, stability, commercial availability and relatively inexpensive cost, in comparison to other carbon-based electrode materials. [88,159] Carbon cloth comprises long individual carbon fibres, between 5 µm and 7 µm in diameter and is produced *via* the thermal decomposition of acrylic. These individual fibres are joined together as a bundle and are then weaved together to produce the carbon cloth [160].

Carbon felt has also been utilised as an electrode material in MFCs. One study has compared the efficacy of carbon felt anodes, using bacteria isolated from sludge from a domestic wastewater plant. The results showed that under anaerobic conditions, a maximum power density of $7.07 \pm 0.45\ mW\ m^{-2}$ was produced [161]. One study, which compared the electrochemical performance of 2D carbon cloth against 3D carbon felt (with spaces between the carbon fibres ranging from *ca.* 20–200 µm), showed that the 2D carbon cloth enhanced the retention of bacteria. A 39.3% microbial volume ratio was demonstrated as opposed to the carbon felt, where bacterial retention was only 16.3% [107]. Denaturing gradient gel electrophoresis analysis determined that *Delftia acidovorans*, *Citrobacter freundii* and *Ochrobactrum intermedium* were isolated from the sludge and that these bacterial species may be potential electrogenic bacterial species [161]. Further, electrochemical analysis of the 2D and 3D carbon cloths showed that the 2D carbon cloth resulted in similar current densities to that of the 3D carbon felt, around $3.5\ A\ m^{-2}$ [107]. This work demonstrated that 2D carbon cloth had promising potential as an electrode material for MFCs, offering a large specific surface area reported to be $\sim 2500\ m^2\ g^{-1}$. Further, there was an increased biocompatibility when compared to the more traditional 3D porous carbon felts [162].

2.5.1.1. Limitations of carbon cloth and felt. There are some limitations of the 3D carbon felt electrode, which were not present in the 2D carbon cloth, such as the clogging of pores. The clogging of pores in 3D porous carbon materials by the entrapment of bacterial cells can ultimately result in cell death. This may lead to a significant reduction of the active electrochemical reaction surface area, as well as a reduction in viable bacteria, thus reducing power outputs [17]. However, limitations have been associated with the use of 2D carbon cloth as an electrode material in MFCs, for example there is a poor reaction start-up [163]. This is often attributed to oxygen crossover from the cathode to the anode which can lead to the inhibition of current production by exoelectrogenic bacteria [163]. Recent research has resolved this problem by using a phosphate buffer to increase the solution conductivity. Further, pre-treating carbon cloth anodes with ammonia gas, was shown to increase the surface charge of the carbon cloths, by increasing the amount of amide groups on the surface [164]. The ammonia treatment of the carbon cloth was shown to increase power production by 48% and reduce start-up time by 50% [164].

2.5.2. Graphite

Graphite has exceptional electrochemical properties, whilst the biocompatibility of graphite has been determined using scanning electron microscopy (SEM), as an abundance of a monoculture biofilm (*E. coli)* can be seen, adhered to a graphitic electrode surface (Fig. 4). A study carried out by Chaudhuri and Lovley, demonstrated that increasing the graphite surface area available for microbial colonisation increased power outputs [165]. This was also demonstrated, when a two chambered MFC was utilised using a pure culture of *Rhodoferax ferrireducens* (anaerobic conditions for the anodic compartment), with excessive amounts of glucose (10 mM) to act as an electron donor. Graphite felt electrodes (with a higher surface area) were compared against graphite rods and a threefold increase in current was produced ($0.57\ mA\ m^{-2}$; 620 mV) [165]. The study also compared porous graphite foam electrodes against the graphite rods. It was demonstrated that even though the geometric surface area was the same, the porous graphite foam produced a 2.4 fold increase in current ($74\ mA\ m^{-2}$; 445 mV), which was attributed to the higher concentrations of cells which were able to adhere to the graphite foam electrodes [165].

2.5.3. Graphene

An example of a new research direction that has the potential to overcome some of the aforementioned issues would be the use of 2D-nanomaterials, such as graphene, as an electrode material/surface coating. Graphene, a two-dimensional (2D) monolayer lattice of sp^2 hybridised carbon atoms, has attracted a plethora of interest in both the scientific and technological communities due to its reported unique properties [166]. Such properties include high physical strength [167], high electron mobility/conductivity at room temperature ($2.5 \times 10^5\ cm^2\ V^{-1}\ s^{-1}$) [168] and a theoretical surface area estimated at $2630\ m^2\ g^{-1}$ [169]. Graphene is also able to sustain extremely high densities of current (reported as one million times higher than copper) [170]. Such properties are ideal for efficient and effective electron transfer, making graphene a prime candidate for use as an electrode material within MFCs.

Graphene has previously been used as the anode material of an MFC with a pure culture of *E. coli* and delivered a maximum power density of $2668\ m\ Wm^{-2}$, which was 18 and 17 times larger than the stainless steel mesh and polytetrafluoroethylene modified electrodes, respectively [171]. Xiao et al. determined the difference between two types of graphene with varying, multilayer morphology (*ca.* 50–100 µm). These graphene sheets were more defective than pristine graphene due to the synthesis method utilised. This involved the thermal annealing of graphene oxide *via* the Hummers' synthesis, and crumpled graphene particles (*ca.* 0.2–5.0 µm) produced *via* an aerosol-assisted capillary compression process [172,173]. These varying graphene morphologies were coated onto carbon cloth electrodes (loading rate: $\sim 5\ mg\ cm^{-2}$) and tested to determine if the difference in surface area/surface roughness had a direct effect on the power density produced by the MFCs [172]. The results showed that modification of the graphene morphology from graphene sheets to crumpled graphene particles led to an increase in both surface area and the power density ($3.6\ W\ m^{-3}$). This was twice that of the activated carbon modified electrode ($1.7\ W\ m^{-3}$) [172].

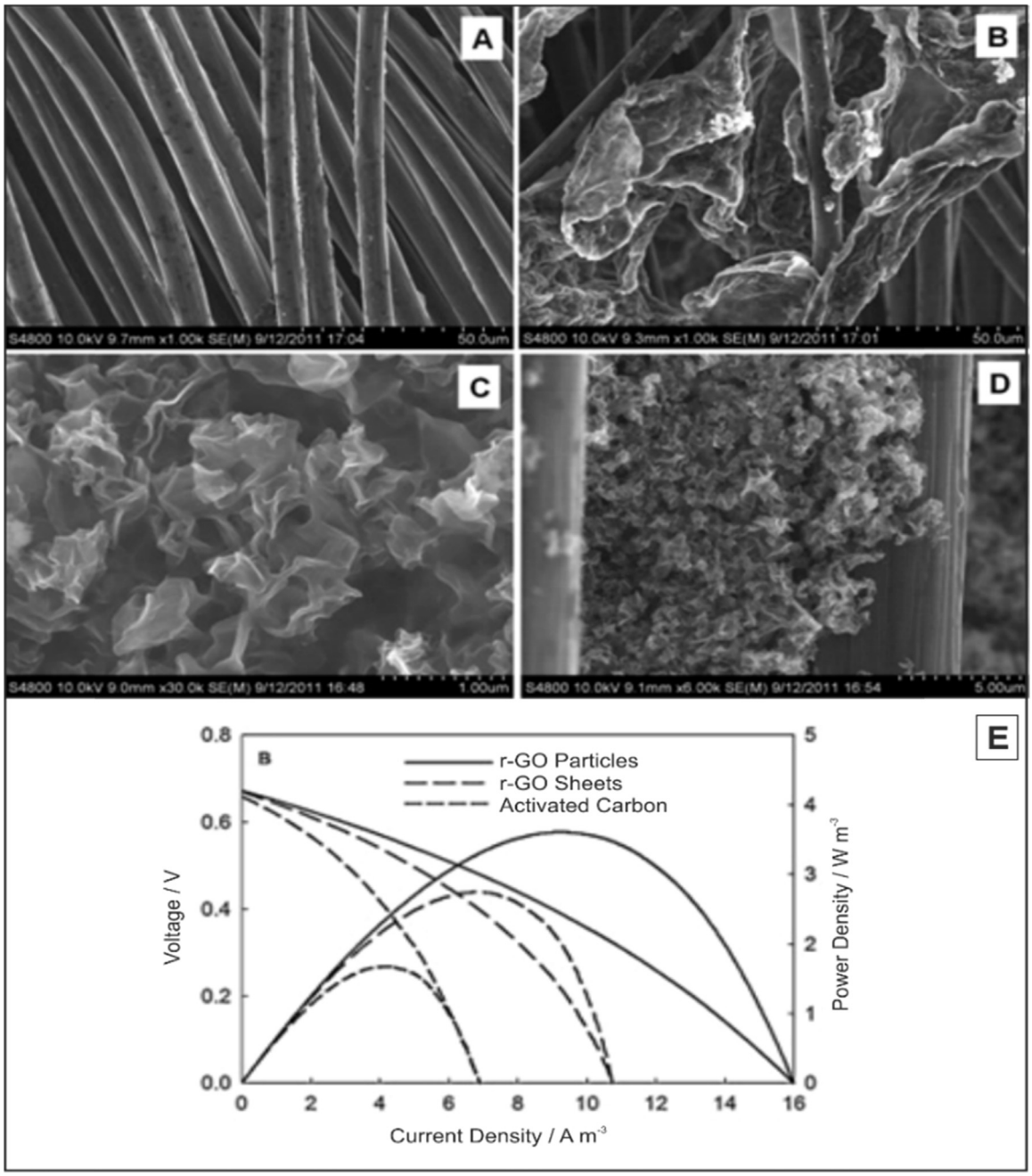

Fig. 5. SEM showing varying morphologies of carbon – based electrodes: (A) carbon fibres in unmodified carbon cloth; (B) regular r-GO sheets deposited on carbon cloth; (C) crumpled r-GO particles before being applied onto carbon cloth; and (D) crumpled r-GO particles stacked on carbon cloth. E) The polarization curves (below the SEM images) show the electricity generation from the carbon - based electrodes, indicating that the reduced graphene oxide particles produced the highest power density, possibly due to the higher electrode surface area as observed in the SEM images (D).
Figure adapted from reference [172].

Fig. 5 offers an insight into this modification of graphene electrode morphology, showing how by increasing the surface area, an increase in the power density may be achieved.

The highest recorded power density produced to date, 5.61 W m^{-2} / 11,220 W m^{-3}, was achieved using a 3D multilayer graphene macroporous scaffold anode. The power density produced a 3.3 fold increase when compared to its planar single-layer 2D control counterparts [174]. Ren et al. demonstrated the ability to produce highly effective MFCs whilst utilising advanced 2D nanomaterials, such as graphene, as the anode/cathode material (Figs. 6 and 7) [174]. It should be noted that the 2D nanomaterials must be correctly analysed and characterised for application as MFC electrodes. Raman spectroscopy is a powerful tool which can be used to effectively identify and characterise the number of layers of graphene-based electrode materials [175]. One of the challenges in the advancement of MFCs for industrial/social end-point applications (*e.g.* wastewater treatment) is both the cost and the reliability. Unfortunately, the production of 2D-nanomaterials such as graphene is unsustainable for this application, however it is expected that as more research is invested into the area of nanomaterials, the production costs will decrease significantly [176].

2.5.4. Carbon nanotubes

Carbon nanotubes (CNTs) are another allotrope of carbon, where the carbon atoms are arranged in hexagons, like graphite. However,

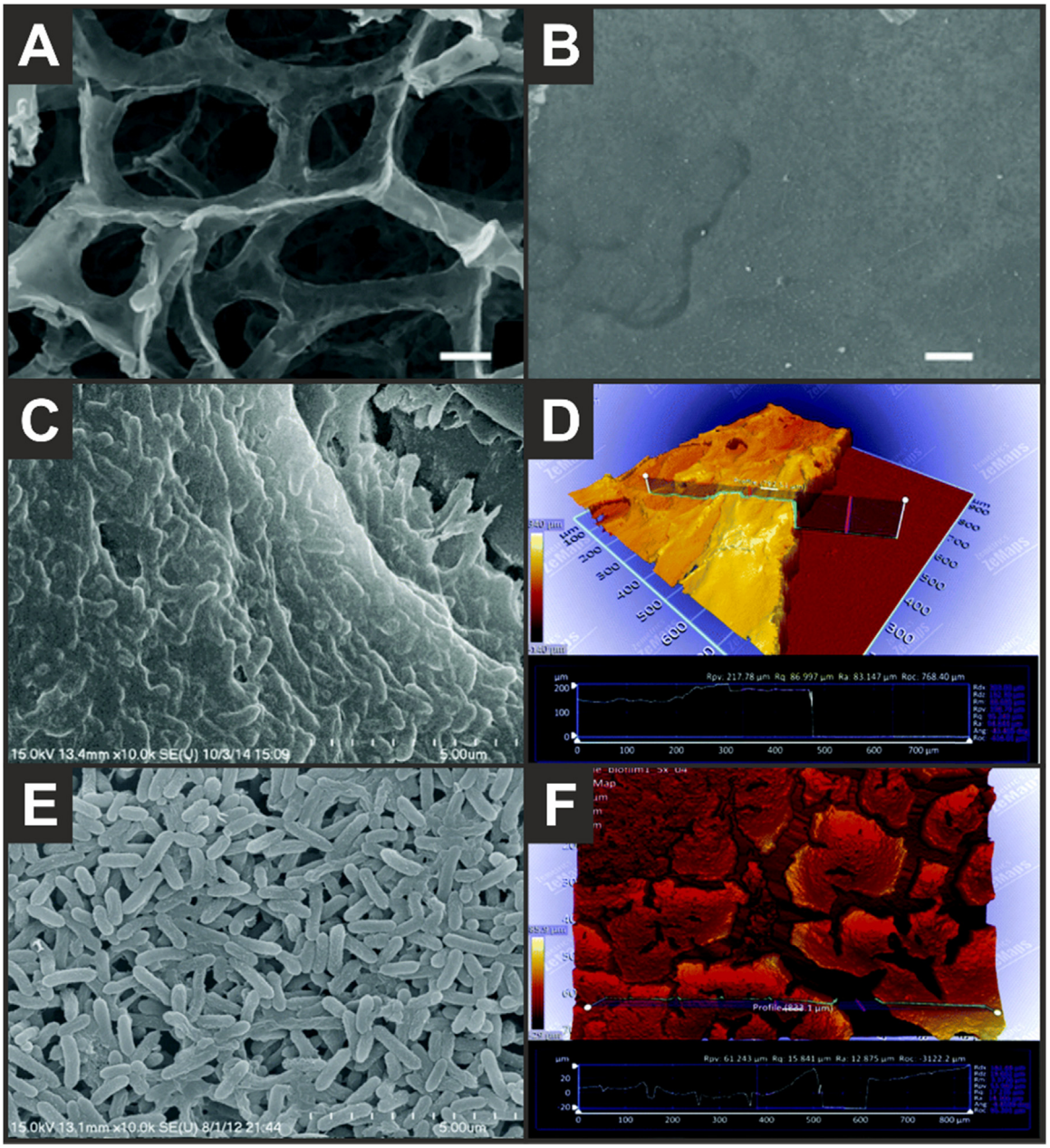

Fig. 6. SEM showing A) 3D graphene macroporous scaffold fabricated *via* chemical vapour deposition, B) monolayer graphene, C) morphology of biofilm adhered to the 3D graphene macroporous scaffold anode and E) morphology of biofilm adhered to monolayer graphene anode. Optical profilometry images of both the 3D graphene macroporous and monolayer anodes with biofilms adhered are shown, D) and F) respectively, this allowed the biofilm thickness to be quantified before SEM was utilised to show morphological differences – C) and E).
Figure adapted from [174].

unlike graphite, the structure of CNTs consist of enrolled tubular graphene in the configuration labelled armchair. This is where the hexagons are orientated parallel to the axis of the nanotube arranged as a seamless cylinder [174,177,178]. CNTs can consist of one or more layers of graphene, which can then be denoted as either single-wall, (SWCNT), or multiwall, (MWCNT), with either open or closed ends [179]. CNTs have demonstrated excellent electrochemical activity due to a variety of factors. These include, their edge plane site/defects to basal plane ratio, chirality, relative size to surface area ratio and nanometre-sized diameter and micrometre-sized length, (where the length of the CNT exceeds the width ratio by one thousand times) [179–181]. SWCNTs and MWCNTs typically have diameters of 0.8–2 nm and 5–20 nm, respectively, although the diameter of MWCNT may exceed 100 nm and have a hollow geometry [179,180].

CNTs have demonstrated enhanced electrochemical performance, in comparison to more traditional electrodes when utilised within MFC technologies [182]. Cyclic voltammetry was utilised to compare the electrochemical activity of a glassy carbon electrode (GCE), with its surface modified with MWCNTs, using *Shewanella oneidensis* [182]. The results found that the use of CNTs raised the current density to 9.70 ± μA cm^{-2}, 82 times greater than the GCE control [182]. This was further confirmed when CNT mat-modified air-cathodes produced a maximum power density of 329 mW m^{-2}, which was more than twice the amount of peak power obtained with carbon cloth cathodes (151 mW m^{-2}) [183].

The activity of single-walled CNTs with carboxyl groups, multi-walled CNTs with carboxyl groups and multi-walled CNTs with hydroxyl-groups as anodes have also been compared [184]. Multi-walled

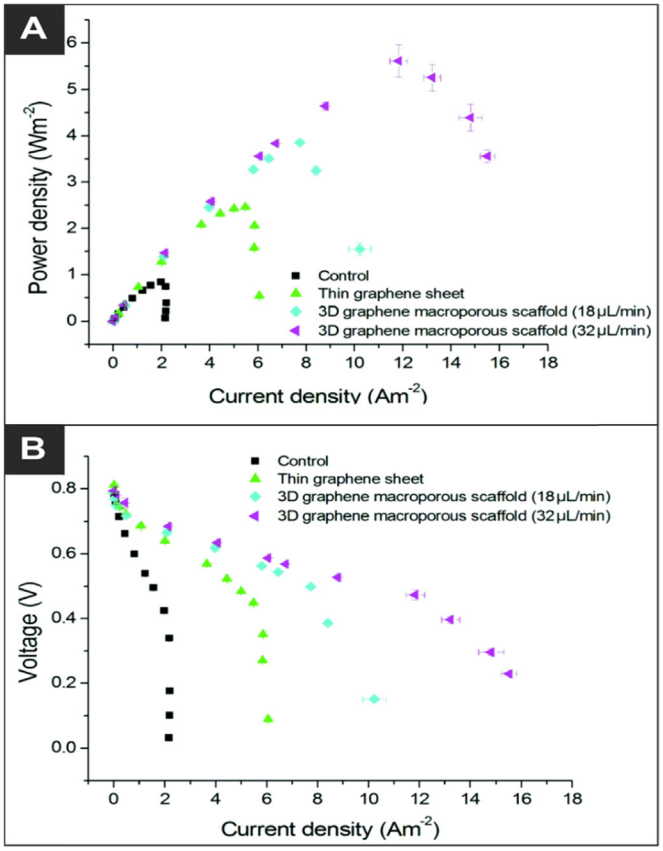

Fig. 7. The MFC with the largest power output reported to date. A) A plot of power density *versus* current density, B) A plot of current density against voltage. Varying anodes were utilised throughout this study: control, 2D single layer graphene, and 3D graphene macroporous scaffold; unless specified, all data collected at 18 µL min^{-1} (*via* flow cell set-up).
Reproduced with permission from [174].

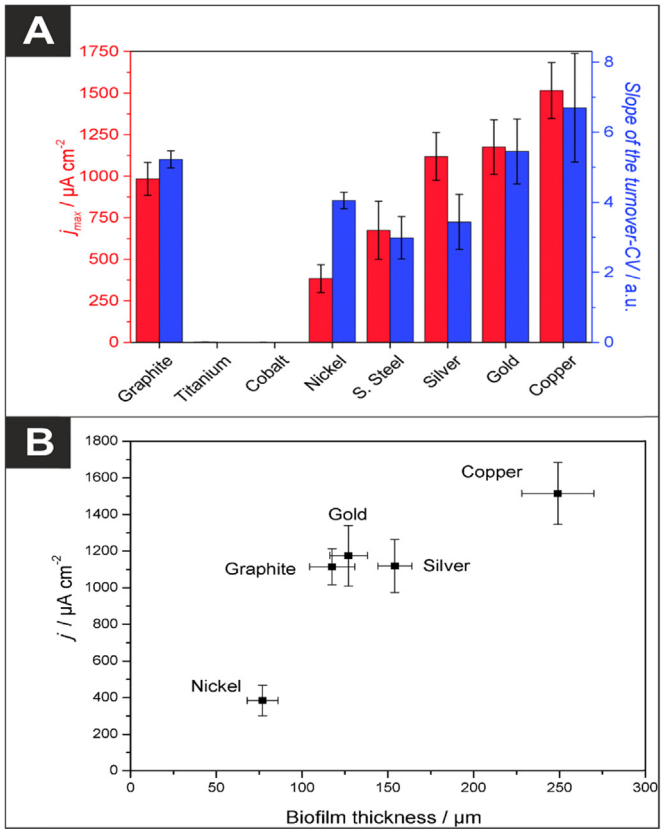

Fig. 8. Comparison of a selection of metal electrodes utilised in MFC configurations compared to a graphite control. A) Electrochemical performance, with the red columns showing average maximum current densities achieved and the blue columns showing the mean values of the slopes of the turnover cyclic voltammograms. B) Correlation of the electro-catalytic current density against biofilm thickness (as determined *via* confocal laser scanning microscopy).
Figure adapted from [189].

CNTs have been reported to provide better results than single-walled CNTs; a power density of 167 mW m^{-2} was achieved by the multi-walled CNT with hydroxyl groups, which was 130% more effective than the carbon cloth control [184]. MWCNTs with hydroxyl functional groups are a possible alternative anode material to traditionally used carbon cloth, due to their greatly improved performance in electron transfer capabilities, microbial attachment and substrate diffusion/oxidation rates [184].

2.6. Non-carbon based electrodes

Despite carbon-based electrodes being the electrode of choice in MFC configurations due to their versatility in structure, non-carbon based electrodes have also been utilised in MFCs. In 2007, Dumas et al. produced a MFC that consisted of a stainless steel anode and cathode. The anode was embedded into marine sediment, which was coupled to the cathode in the overlying seawater [84]. The maximum power density produced by this SMFC configuration resulted in a lower output (4 mW m^{-2}) than the laboratory control (23 mW m^{-2}) [84]. It was suggested that this might be due to biofilm damage on the cathode, due to grazing fish and possible damage to electrical connections by waves [84]. These results can be compared against carbon-based electrodes utilised within SMFCs (with similar-sized anodes: ~ 0.18 m^2) with a graphite plate anode with a stainless steel cathode (12 mW m^{-2}), plain graphite electrodes (28 mW m^{-2}) and a single graphite rod anode with a carbon brush cathode (34 mW m^{-2}) [84,185–187].

Commercial platinum-coated titanium metal (deposited by electroplating) and uncoated titanium have also been trailed as non-porous bioanodes, and were compared against flat and roughened graphite [188]. Polarization curves and impedance spectroscopy showed that bioanode performance decreased in the order roughened graphite > platinum coated titanium > flat graphite > uncoated titanium [188]. The uncoated titanium anode produced the lowest current, whilst the anode potential was considerably higher than the other electrodes (> −150 mV *vs.* Ag/AgCl at $R = 1000\ \Omega$) [188]. This result may have been due to anodic passivation of the titanium, suggesting that uncoated titanium is an unsuitable anode material for MFC set-ups [188].

A study by Baudler et al. in 2015compared the performance of gold, silver, copper, nickel, cobalt and titanium electrodes against a graphitic benchmark (Fig. 8) [189]. The average maximum current densities demonstrated that of the three most noble metals, copper produced the highest maximum current density (1515 µA cm^{-2}), followed by gold (1175 µA cm^{-2}) and silver (1119 µA cm^{-2}), which were slightly higher than that of the graphite control (984 µA cm^{-2}) [189]. The results for silver and copper are surprising, as these metals are well established in their application as antimicrobial metals, and have been studied extensively *i.e.* for implementation as surface coatings for medical devices/equipment [190–192]. However, it was demonstrated that electrochemically active, electrode respiring bacteria from secondary biofilms (which are highly *Geobacter* dominated) have the ability to adhere to, colonise and form highly active biofilms on both copper and silver electrodes. These produced biofilm thicknesses of 249 ± 21 µm and 154 ± 10 µm, respectively [189]. In light of this, copper and silver electrodes could play a pivotal role in the optimisation of MFCs. Of the non-noble metals (titanium, cobalt, nickel and stainless steel) stainless steel produced the highest average maximum current density

($674\ \mu A\ cm^{-2}$) followed by nickel ($384\ \mu A\ cm^{-2}$). However, the current densities produced by cobalt and titanium were negligible in comparison to the other electrode materials [189]. This marked decrease in current density by the non-noble metals may be attributed to the formation of metal oxides, acting as a barrier in charge transfer processes between the biofilms and the metals [189,193].

The suitability of gold electrodes for use within MFCs has also demonstrated by Ritcher et al. which were used in conjunction with *G. sulfurreducens* (ATCC 51573), with 10 mM acetate as the electron donor and 40 mM fumarate as the electron acceptor [194]. The results showed that the current stabilised at 0.4–0.7 mA after *ca.* 6 – 10 days and that this maximum current was comparable to carbon fibre anodes under the same conditions [194,195]. The ability to transfer electrons to the gold anode was postulated to be due to the direct contact between *G. sulfurreducens via* micro-nanowires (pili). However, work by others has suggested that using gold electrodes with *Shewanella putrefaciens,* was not suitable for use within MFCs [196]. A possible explanation for this variation in electrochemical response between the bacterial species' could be due to the differences in electron transfer mechanisms, as *G. sulfurreducens* is associated with direct electron transfer, whilst *S. putrefaciens* is associated with redox proteins displayed on the surface of bacterial cells, such as c-type cytochromes [60,194,197]. Thus, the interactions of the different electrochemical pathways of the bacteria with the surfaces may have resulted in the conflicting results.

3. Mechanisms of electron transport

Exoelectrogenic bacterial species have the ability to facilitate electron transfer *via* two mechanisms, direct and indirect electron transfer [198]. Direct electron transfer requires a physical connection between the bacterial cell and the electrode surface, namely nanowires and/or redox-active proteins. Indirect electron transfer does not require a physical connection but instead this mechanism relies on electron shuttling molecules [199]. There are currently 3 established methods of electron transfer (*e.g.* nanowires, membrane bound cytochromes and electron mediators) which bacteria can utilise to donate electrons to the anode in a MFC configuration (Fig. 9) [200].

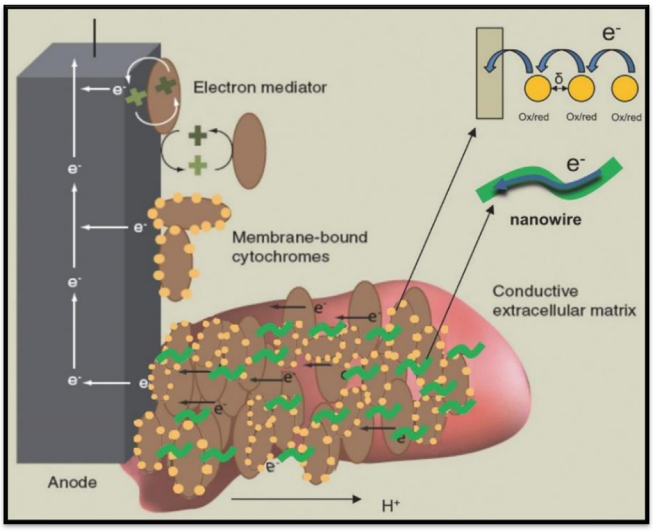

Fig. 9. Three methods of electron transfer demonstrated by exoelectrogenic bacteria, including; direct electron transfer – conductive pili denoted within the literature as nanowires and redox-active proteins, and indirect electron transfer by electron shuttles.
Reproduced with permission from [200].

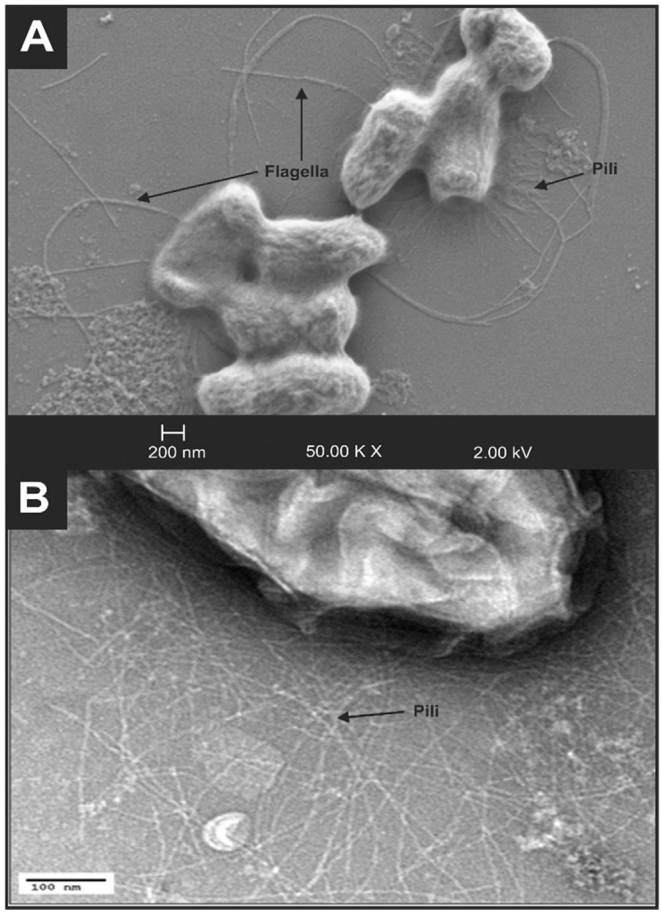

Fig. 10. A) SEM showing the difference in morphology of flagella and pili on the surface of *E. coli.* Due to this distinct difference in properties, we propose the terms "micro-nanowires" and "macro-nanowires" in order to describe pili and flagella, respectively, in terms of electron transfer properties in MFC configurations. Section A image, courtesy of Whitehead et al. MMU, UK. B) Transmission electron microscopy showing *G. sulfurreducens* strain GUP, (top part of the image), expressing abundant micro-nanowires. This allows the bacteria to reduce metals, such as iron oxide, and donate electrons to the anode in a MFC set-up.
Section B, adapted from [208].

3.1. Direct electron transfer via conductive pili

Bacterial colonies isolated in the anodic chamber of a fuel cell are incapable of transferring electrons directly to the electrode [1]. However, anodophiles have the ability to use electrons (in the anode) as their end electron acceptor. Thus, these specific bacterial species are involved in electron transfer, leading to the generation of an electrical charge [201]. A major breakthrough in MFC technology was observed by Kim et al. who demonstrated that electron transfer does not always need mediator (electron transfer) compound molecules [157]. The bacterial cell surface of specific isolated bacterial species, such as *Shewanella* spp., and *Geobacter* spp., have micrometre long proteinaceous filaments that extend from their outer surface into the extracellular matrix. These appendages are thought to be involved in extracellular electron transport processes, referred to as microbial nanowires – due to their long filament-like appearance and conductive attributes [202].

Nanowires can be either flagella or pili, both of which have very distinct properties, and therefore we propose the terms micro-nanowires and macro-nanowires (Fig. 10). Traditionally, the major role of the flagellum of bacteria is to mediate the motility of the cell *via* swarming and swimming, allowing for colony expansion on a surface. One of the roles of Type IV pili is to mediate twitching to pull the cell

across a surface (often in dense aggregates) [203]. Nanowires have the ability to partake in direct electron mediated transfer. Type IV pili play vital roles in secretion systems for effectors, microbial adherence and bacterial movement, establishing contact between the bacterial species and the electrode surface [204]. Reguera et al. showed that wild type *G. sulfurreducens* could attach to Fe(III) oxides after 48 h, as demonstrated by an increase in biomass. However, in the same time period, the *pilA*-deficient strain could not grow, which was indicated by a decrease in biomass [205]. In regards to the bacterial species evaluated for electricity generation for potential application in microbial fuel cell technologies, *G. sulfurreducens* is currently the "gold standard", producing the highest recorded current densities of any known pure culture, utilising micro-nanowires (Fig. 10) [206–208].

G. sulfurreducens is a Gram – negative, δ-proteobacterium, and is a rod shaped, non-fermentative, obligate anaerobe, with flagella and type IV pili production. *G. sulfurreducens* is able to generate energy in the form of adenosine triphosphate, due to its ability to reduce metals such as Fe(III), by using metal ion-mediated electron transport mechanisms to oxidise organic compounds to CO_2 [209]. The electrically conductive pili of *G. sulfurreducens* play a pivotal role in long-range electron transfer. Pilus conductivity is dependent upon pH levels, with a reduction in conductivity observed in a higher pH (pH 10) - 37 ± 15 μS cm^{-1}. However, a marked increase was noted at pH 2, where the electrical conductivity of 188 ± 33 mS cm^{-1} was also produced from individual pili [210].

It is thought that the reduction of iron (and other metal) oxides by *G. sulfurreducens* requires direct contact between the bacteria and the Fe (III) oxides. This is in order to reduce equivalents from the tricarboxylic acid cycle (TCA), also known as the Krebs cycle [211]. This ability to locate (*via* chemotaxis) and reduce Fe(III) oxides in order to use them as terminal electron acceptors is advantageous in subsurface environments due to the abundance of Fe(III) oxides [209,212]. Both nicotinamide adenine dinucleotide phosphate (NADPH) and nicotinamide adenine dinucleotide (NADH) have the capability to transfer reducing equivalents to the electron transport chain, during fumarate reduction by *G. sulfurreducens.* This provides a source of ATP from the iron oxides [211].

The current density generated by a monolayer of planktonic cells attached to the surface of an electrode is limited by the surface area of the electrode. It is thought that this is presumably due to a lack of available space for the nanowires to adhere to, thus leading to a reduction in direct electron transfer [213]. Therefore, it is of little surprise that conductive biofilms (which are many layers thick) have the ability to produce much higher power and current densities, due to multiple layers of bacteria contributing to the overall net energy generation. Friman et al. described a current generation (under a constant external resistor of 1 kΩ) of 125 mA m^{-2} from planktonic cells as opposed to 541 mA m^{-2} from an established biofilm, where acetate was used as the substrate with a pure culture of *Cupriavidus basilensis* [213]. Conductivity measurements with *G. sulfurreducens* in biofilm formulations have shown high conductivities, even rivalling those of synthetic conductive polymers [207]. *G. sulfurreducens,* in multi-layered biofilms of an average height of 40 μm (± 6 μm), produced a maximum current of 12 mA, while the planktonic cells produced a maximum current of 2.5 mA, [205] after 4 days of incubation using a continuous batch method [214].

3.2. Direct electron transfer via redox-active proteins

Most studies suggest that the direct contact by pili of the conductive bacterial biofilms and the iron oxides is essential for the reduction of iron oxides. However, another mechanism of electron transfer requires redox active proteins and allows for short-range electron transfer to take place [215]. *C*-type cytochromes are commonly known for their primary function in mitochondria, as these molecules play a pivotal role in ATP synthesis [216]. Smith et al. revealed that deletion of the gene encoding for PilA, a structural pilin protein in the KN400 strain of *G. sulfurreducens* inhibited iron oxide reduction [217]. One possible explanation for the continued iron reduction even with structurally damaged pili is the utilisation of *c*-type cytochromes, such as OmcS and OmcE [218].

C-type cytochromes were found in abundance on the surface of *G. sulfurreducens* cells, with OmcS and OmcE being the most commonly isolated. It has been shown that when either *omcS* or *omcE* genes were deleted, reduction of iron (III) oxides could no longer take place [219]. Immunolocalization and proteolysis studies have also demonstrated that the cytochrome, OmcB is essential for optimal Fe (III) reductions, it is both highly expressed during growth upon electrode surfaces and is embedded in the outer membrane of the cell [220–222]. It has been suggested that bacteria such as *G. sulfurreducens* developed this ability to reduce metal oxides such as iron, due to being isolated in harsh environments surrounded by large quantities of insoluble materials. Therefore, natural selection and evolution have led to the production of effective strategies to overcome the lack of ATP production that is usually achieved by more conventional methods, *i.e.* aerobic respiration [223,224]. Thus, the genome of *G. sulfurreducens* gained the ability to reduce iron oxides due to selection pressure. Therefore, it may be speculated that such mutations may lead to improved degradation of iron oxides, in order to increase ATP production [225,226].

3.3. In-direct electron transfer via electron shuttles

Bacteria can generate electricity due to the production of secondary metabolites, which are able to act as endogenous redox mediators, often referred to as electron shuttles. Electron shuttles are organic molecules with a low molecular weight that have the ability to catalyse both reduction and oxidation reactions, using for example phenazines and quinones [227]. Bacterial cells can utilise both added/in solution (exogenous) or self-produced/on bacterial cell surface (endogenous) shuttle compounds for extracellular electron transfer. However, for effective electron transfer to take place, electron shuttles must be both chemically-stable and not easily biologically degraded (Fig. 11) [227].

Unlike conductive pili, electron shuttles eliminate the need of direct contact between the bacterial cell and the electron acceptor (which in the case of MFCs is the electrodes) [202]. Within the bacterial cells, electrons are first transported to the cell surface *via* a metabolic pathway, which involves redox-active proteins and low molecular weight compounds. Subsequently, electrons are then transported to cytochromes or potential shuttles in either the periplasm or the outer-membrane [227]. Soluble electron shuttles can diffuse into the medium surrounding the bacterial cell, and once outside, the electrons can be transferred to suitable external acceptors, with examples including

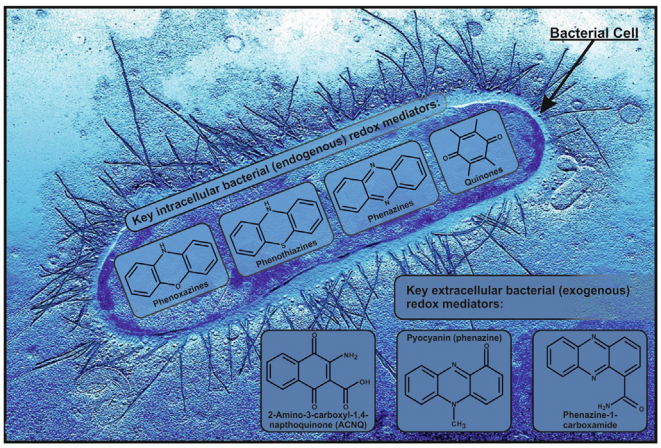

Fig. 11. Exogenous and endogenous redox mediators, capable of partaking in electron transfer [297].

insoluble Fe (III) oxides or a MFC anode [227]. Some compounds shown to be effective electron shuttles include thionine, methyl viologen, 2-hydroxy-1,4-naphtoquinone, methylene blue, humic acids and anthraquinone-2,6-disulfonic acid [228–231]. Other more common examples of electron shuttles are molecules known as flavins.

Flavins demonstrate enhanced efficiency when partaking in biogeochemical iron cycles, and redox potentials, which improves electron transfer. Thus, flavins have the potential to be applied to MFC technologies as such molecules can be used as endogenous electron transfer mediators [232]. Further, the importance of flavins as electron shuttles, have been shown, as the concentration of flavins increased from 0.2 μm to 0.6 μm to 4.5–5.5 μm the peak current produced by *S. oneidensis* became four times greater [227].

Flavins are often produced as secondary metabolites in bacteria, for example, riboflavin which is also known as vitamin B2. This compound has been shown to act as an electron shuttle by Marsili et al. when *S. oneidensis* biofilms were analysed [233]. Results showed that the removal of riboflavin from biofilms resulted in a reduction of electron transfer rate to the electrodes by more than 70% [233]. Another example of a flavin is pyocyanin, this has been shown to mediate electron transfer in MFCs [234]. The concentration of pyocyanin in an anodic culture has shown a direct correlation to power generation efficiency, due to its ability to transport electrons through the cell membrane [235]. Pyocyanin is produced as a secondary metabolite by *Pseudomonas aeruginosa*, it is a water-soluble blue green phenazine compound, responsible for the green pigmentation often associated with infected wounds [236]. The production of pyocyanin by *P. aeruginosa* is of paramount importance due to its versatile nature. Pyocyanin has multiple functions including antimicrobial activity against a range of microorganisms (including bacteria, fungi and protozoa), an electron shuttle and a key sensing molecule to upregulate the transcription of quorum sensing genes, leading to biofilm formation [237–245].

3.4. Mixed community microbial fuel cells

The different mechanisms in which bacteria can facilitate electron transfer has been considered, however, few monoculture strains have the capacity to produce power densities as great as strains that are inoculated in mixed communities. For example, enriched anodic biofilms have previously been shown to generate power densities as high as 6.9 W per m^2 (projected anodic area) [25]. Some bacteria found in MFC biofilms have shown that the cells do not interact directly with the anode, however through interactions with other bacteria they can still contribute indirectly to the production of electricity. One example of this has been demonstrated by *Brevibacillus* spp., (strain PTH1), which was found in abundance in a MFC community. Power production from this bacterial subclass alone is low, however when co-cultured with *Pseudomonas* spp., (or supernatant from an MFC community containing *Pseudomonas* spp.,) there was a marked increase in electricity generation [246].

Specific members of fluorescent *Pseudomonads* can produce and secreet phenazines *i.e.* pyocyanin production by *P. aeruginosa* strains [243]. The effect of pyocyanin addition to non-pyocyanin producing MFC biofilms has shown varying results. Rabaey et al. demonstrated that the addition of pyocyanin to a pure culture of *Enterococcus faecium* (strain KRA3), led to a peak power increase from 294 ± 49 μW m^{-2} to 3977 ± 612 μW m^{-2}, a 13-fold increase [246]. However, against *E. coli* (ATCC 4157), the power output showed a reduction by 50%, after the addition of pyocyanin (117 ± 16 μW m^{-2} to 50 ± 53 μW m^{-2} [246]. A possible explanation for this could be due to the selective antimicrobial activity of redox-active proteins such as pyocyanin [237,238]. Pyocyanin, has shown greater antimicrobial activity against aerobic bacterial strains; in 1981 Baron and Rowe showed that facultative anaerobes were two-fold (or more) resistant [237]. The addition of pyocyanin (or pyocyanin producing strains of bacteria *e.g. P. aeruginosa*) to non-pyocyanin producing biofilms could therefore be used to increase power outputs. One example, where this approach could be applied is the degradation of waste/toxic matter (such as toluene) to efficiently convert organic matter to electricity in a MFC set-up [247]. However, significance should be placed upon the selection of bacteria utilised within mixed community biofilms MFC configurations, ensuring resistance to the antimicrobial effects of exogenous redox mediators.

The interactions of mixed community biofilms is complex and is yet to be fully understood. However, the use of mixed community biofilms, both inter-bacterial and other microorganisms (*i.e.* fungi such as yeast) for MFCs, has vast potential. A pure culture MFC (*G. sulfurreducens*) was shown to produce a maximum power of 461 ± 8 mW m^{-2}, compared to a mixed community biofilm MFC that produced a maximum power of 576 ± 25 mW m^{-2} under the same conditions [248]. Another study, which used the fungus *Trametes versicolor* and *S. oneidensis* in combination, showed that the bacterial-fungal interactions enhanced power generation, producing a maximum power density of 0.78 W m^{-3} [249]. Fernández de Dios et al. suggested that the bacterium was capable of both adhering to and transporting electrons from the *T. versicolor* filamentous networks. Further, *T. versicolor* can produce oxidative enzymes, which provide an oxidoreductase mechanism, which involves the transportation of electrons from donor to acceptor [249]. Clearly mixed biofilm communities, that have the ability to generate electricity by more than one mechanism, will play a pivotal role in the improvement of MFCs [250].

4. Field standardisation and comparison techniques

Differences in MFC configurations, including architectures, anode/cathode/PEM materials and solution chemistries have hindered the progression of MFC technologies, due to the lack of direct comparisons of power production available [117]. In the late 1980′s, Bennetto et al. studied synthetic mediators, and this resulted in the development of the “analytical MFC” that is still used by a number of research groups to date [35,251]. Furthermore, over the last decade researchers have also started to use another MFC design whilst carrying out experiments [88,117,252–256]. This design utilises a single-chamber cube shaped MFC (4 cm) with a 3 cm (diameter) analyte chamber, a graphite fibre brush anode and a platinum cathode catalyst [117]. This configuration usually uses 50 mM phosphate buffer solution and acetate as a fuel source [117]. The use of identical MFC designs and conditions throughout the field allows for direct comparisons between energy-generation results from a wide array of laboratories [117]. In order to improve power outputs from MFC technologies, the design of the MFCs need to be detailed (*e.g.* distance between electrodes, PEM type *etc.)*, allowing for appropriate comparisons and identification of factors capable of improving energy generation.

One issue that greatly hinders the advancement of MFC technologies is the lack of consistency and standardisation in regards to stringent comparisons of energy outputs of MFCs (Table 1) [257]. Current density is the most typically used performance indicator of MFCs at a set potential which is typically calculated in watts per square meter (W m^{-2}), and measures power output in relation to the surface area of the anode [257,258]. However, the use of surface based power density has many limitations, making it unsuitable for measuring MFC energy generation. One major limitation is that it is difficult to measure the exact surface area of porous electrodes, and therefore it is often estimated as the projected surface area [257]. Further, surface areas of porous electrodes of identical size could vary drastically between similar electrodes [257]. Another way to quantify energy outputs from MFCs is watts per cubic meter (W m^{-3}), which takes into account the anode liquid volume but excludes variation in the electrode size and configuration [257]. Traditional performance indicators such as current/power density, resistance, impedance and capacitance testing can all provide vital information [259]. Ge et al. proposed a new parameter in order to effectively describe energy generation from MFCs, and this

term is the normalised energy recovery (NER), which gives energy generation in kWh m^{-3} [257,260]:

$$NER = \frac{power \times time \quad (t)}{wastewater\ volume \quad (treated\ within\ time \quad (t))} = \frac{Power}{wastewater\ flow\ rate} \tag{3}$$

However, this calculation assumes that all MFC technologies are wastewater treatment systems but this is not the case [260]. Eq. (3) can be modified in order to take into account the organic substrates present in solution, based on the removed chemical oxygen demand (COD) in kilowatt hours per kilogram of COD [kWh (kg COD)$^{-1}$] [257]:

$$NER = \frac{power \times time \quad (t)}{COD \quad (removed\ within\ time \quad (t))} = \frac{power}{wastewater\ flow\ rate \times \Delta COD} \tag{4}$$

Such performance power indicators will allow for a better understanding of organic compound conversion to energy *via* MFCs.

5. Conclusions

MFC technologies have the potential to play a pivotal role in the transition from fossil fuel based technologies to more renewable energy sources. Research into this area is clearly progressing but there is still much more to do in order for MFC technologies to be routinely adapted into industry and society. This review provides an overview of MFC technologies thus far, whilst benchmarking MFC performance and limitations. Currently the highest power output from an MFC is comparable to that of a PEM hydrogen fuel cell; however, further progression of this field is expected. This expected advancement will be due to the optimisation and tailored development of individual parameters such as, enhanced electrode materials that are more suitable for this application. This, alongside interdisciplinary research intoexoelectrogenic bacteria, their biochemical pathways and the influence of secondary metabolites that underpin electron transfer mechanisms, could lead to power outputs much closer to that of the theoretical limits, as well as furthering the advancing field of electromicrobiology.

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Conflicts of interest

The authors declare they have no competing interests.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.rser.2018.09.044.

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